

Generalized density functional theory for degenerate states

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An extension of density functional theory is proposed for degenerate states. There are suitably selected basic variables beyond the subspace density. Generalized Kohn–Sham equations are derived. A direct method is proposed to ensure the fixed value of ensemble quantities. Then the Kohn–Sham equations are similar to the conventional Kohn–Sham equations. But the Kohn–Sham potential is different for different ensembles. A simple local expression is proposed for the correlation energy. © 2005 American Institute of Physics. [DOI: 10.1063/1.1871933]

I. INTRODUCTION

In a couple of recent papers¹ it was shown that it is possible to choose arbitrary physical quantities as basic variables to determine the ground-state properties of the system. An approach presented by Nagy and Parr in the local thermodynamical formalism² can be considered a special case of this general approach. Recently, Becke³ and Maximoff *et al.*⁴ treated degenerate states by a method that can also be regarded a special case of the theory of Higuchi and Higuchi.¹ Here, an extension of this general theory is proposed for degenerate states.

II. GENERALIZED HOHENBERG–KOHN THEOREM FOR A DEGENERATE STATE

In an earlier paper one of the authors⁵ proposed a formalism for degenerate states. Now, we extend this theory into a more general one.

Consider the lowest-lying solutions of the Schrödinger equation

$$\hat{H}|\Psi_\gamma^\Gamma\rangle = E_0^\Gamma|\Psi_\gamma^\Gamma\rangle \quad (\gamma = 1, 2, \dots, g_\Gamma), \quad (1)$$

where g_Γ is the degeneracy. (Only one index is used to denote the symmetry both in spin and ordinary space.) The subscript 0 in the energy shows that only the lowest-lying solution of symmetry Γ is regarded. The space of all antisymmetric wave functions is divided into disjoint subspaces with different symmetries. The constrained-search technique is applied over a subspace S^Γ . The dimension of the subspace is equal to the degeneracy g_Γ .

The subspace density is defined by

$$n^\Gamma = \sum_{\gamma=1}^{g_\Gamma} w_\gamma \int |\Psi_\gamma^\Gamma|^2 ds_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N, \quad (2)$$

where \mathbf{x} stands for both the coordinates and the spin. The weighting factors w_γ should satisfy the conditions

$$1 = \sum_{\gamma=1}^{g_\Gamma} w_\gamma \quad (3)$$

and

$$w_\gamma \geq 0. \quad (4)$$

The superscript Γ in n^Γ denotes that it is constructed from wave functions that belong to the subspace S^Γ . The subspace densities do not generally have the symmetry Γ . Their symmetry depends on the weighting factors w_γ too. In principle, any set of weighting factors w_γ satisfying conditions (3) and (4) can be used. It was shown that if the weighting factors w_γ are all equal, the subspace density has the symmetry of the external potential. So, for instance, for atoms the subspace density is spherically symmetric. The subspace density matrix is defined as

$$\hat{D}^\Gamma = \sum_{\gamma=1}^{g_\Gamma} w_\gamma |\Psi_\gamma^\Gamma\rangle \langle \Psi_\gamma^\Gamma|. \quad (5)$$

Let \mathbf{X} denote suitably selected quantity or quantities.¹ The subspace average can be given by

$$\mathbf{X}^\Gamma = \sum_{\gamma=1}^{g_\Gamma} w_\gamma \langle \Psi_\gamma^\Gamma | \hat{\mathbf{X}} | \Psi_\gamma^\Gamma \rangle, \quad (6)$$

where $\hat{\mathbf{X}}$ is the corresponding operator(s). In the following we omit the superscript Γ to make the notation simpler. (We are always treating a given symmetry.)

Now the constrained search leads to

$$\begin{aligned}
 E[n, \mathbf{X}] &= \min_S \sum_{\gamma=1}^g w_{\gamma} \langle \Psi_{\gamma} | \hat{H} | \Psi_{\gamma} \rangle \\
 &= \min_{n, \mathbf{X}} \left\{ \min_{S \rightarrow (n, \mathbf{X})} \sum_{\gamma=1}^g w_{\gamma} \langle \Psi_{\gamma} | \hat{H} | \Psi_{\gamma} \rangle \right\} \\
 &= \min_{n, \mathbf{X}} \left\{ F[n, \mathbf{X}] + \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \right\}, \quad (7)
 \end{aligned}$$

where the universal functional $F[n, \mathbf{X}]$ is defined as

$$F[n, \mathbf{X}] = \min_{S \rightarrow (n, \mathbf{X})} \sum_{\gamma=1}^g w_{\gamma} \langle \Psi_{\gamma} | \hat{T} + \hat{V}_{ee} | \Psi_{\gamma} \rangle. \quad (8)$$

\hat{T} and \hat{V}_{ee} are, respectively, the kinetic and the electron-electron repulsion operators. $v(\mathbf{r})$ denotes the local external potential.

Then the generalized Hohenberg–Kohn theorem has the form

$$F[n, \mathbf{X}] + \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \geq E_0, \quad (9)$$

which can be readily proved as follows:

$$\begin{aligned}
 F[n, \mathbf{X}] + \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \\
 &= \min_{S \rightarrow (n, \mathbf{X})} \text{tr} \{ \hat{D}(\hat{T} + \hat{V}_{ee}) \} + \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \\
 &= \min_{S \rightarrow (n, \mathbf{X})} \text{tr} \{ \hat{D}(\hat{T} + \hat{V} + \hat{V}_{ee}) \} \geq E_0, \quad (10)
 \end{aligned}$$

where the last inequality follows from the variational principle. The variational principle is valid here because lowest-lying energy level of a given symmetry is taken. There is an equality if and only if the trial quantities n and \mathbf{X} are equal to the true quantities n_0 and \mathbf{X}_0 .

III. GENERALIZED KOHN–SHAM EQUATIONS FOR A DEGENERATE STATE

The generalized Kohn–Sham equations can be derived by minimizing the kinetic energy keeping the ensemble quantities $n(\mathbf{r})$ and \mathbf{X} fixed. The kinetic energy functional is defined as

$$T_s[n, \mathbf{X}] = \min_{S \rightarrow (n, \mathbf{X})} \sum_{\gamma=1}^{g^0} w_{\gamma} \langle \Psi_{\gamma}^0 | \hat{T} | \Psi_{\gamma}^0 \rangle, \quad (11)$$

where the superscript 0 refers to the noninteracting system. The following step is to express the ensemble quantities with the orbitals. As we have a degenerate state the wave function cannot be given by a single Slater determinant even in the noninteracting case. A linear combination of Slater determinants Φ has to be taken:

$$\Psi_{\gamma}^0 = \sum_j c_j^{\gamma} \Phi_j^{\gamma}. \quad (12)$$

Because of the normalization of the wave function Ψ_{γ}^0 ,

$$\sum_j^{g^0} |c_j^{\gamma}|^2 = 1. \quad (13)$$

Let ϕ_i denote the orbitals. The density obtained from the wave function Ψ_{γ}^0 is given by

$$\begin{aligned}
 n_{\gamma} &= N \int |\Psi_{\gamma}^0|^2 d\mathbf{x}_2 \cdots d\mathbf{x}_N d\sigma \\
 &= N \int \sum_j^{g^0} \sum_{j'=1}^{g^0} c_j^{\gamma*} c_{j'}^{\gamma} \Phi_j^{\gamma*} \Phi_{j'}^{\gamma} d\mathbf{x}_2 \cdots d\mathbf{x}_N d\sigma \\
 &= N \int \sum_j^{g^0} |c_j^{\gamma}|^2 |\Phi_j^{\gamma}|^2 d\mathbf{x}_2 \cdots d\mathbf{x}_N d\sigma. \quad (14)
 \end{aligned}$$

One can immediately notice that there is no contribution from the product of different determinants. If two determinants differ only in one orbital there might be a contribution; however, it has different symmetry and corresponds to some γ' different from γ :

$$n_{\gamma} = \sum_j^{g^0} |c_j^{\gamma}|^2 \left(2 \sum_{i=1}^{N_c} |\phi_i|^2 + \sum_{i=N_c+1}^M |\phi_i|^2 \Theta_{ji}^{\gamma} \right). \quad (15)$$

Orbitals in closed shells are doubly occupied. Θ_{ji}^{γ} is 1 if the orbital ϕ_i occurs in the determinant Φ_j^{γ} , otherwise 0. The ensemble density has the form

$$n = \sum_{\gamma} w_{\gamma} n_{\gamma}. \quad (16)$$

Taking all w_{γ} equal we obtain

$$\begin{aligned}
 n &= \sum_{\gamma} \sum_{j=1}^{g^0} |c_j^{\gamma}|^2 \left(2 \sum_{i=1}^{N_c} |\phi_i|^2 + \sum_{i=N_c+1}^M |\phi_i|^2 \Theta_{ji}^{\gamma} \right) \\
 &= 2 \sum_{i=1}^{N_c} |\phi_i|^2 + \sum_{i=N_c+1}^M \lambda_i |\phi_i|^2, \quad (17)
 \end{aligned}$$

where the occupation numbers are

$$\lambda_i = \sum_j \sum_{\gamma=1}^{g^0} |c_j^{\gamma}|^2 \Theta_{ji}^{\gamma}. \quad (18)$$

The noninteracting kinetic energy can be written as

$$T_s = -\frac{1}{2} \sum_i \lambda_i \int \phi_i^* \nabla^2 \phi_i, \quad (19)$$

where $\lambda_i=2$ for the closed shells. The ensemble quantity \mathbf{X} should also be expressed with the orbitals. To obtain the generalized Kohn–Sham equations the noninteracting kinetic energy is minimized with the conditions that the ensemble quantities n and \mathbf{X} are fixed and the orbitals are orthonormals,

$$T_s - \int \Lambda(\mathbf{r}) \left(n(\mathbf{r}) d\mathbf{r} - \sum_i \lambda_i |\phi_i(\mathbf{r})|^2 \right) - \int \mu(\mathbf{r}) \{ \mathbf{X}(\mathbf{r}) - \mathbf{X}[\phi_i(\mathbf{r})] \} - \sum_{i,j} \epsilon_{ij} \left(\delta_{ij} - \int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} \right), \quad (20)$$

where $\Lambda(\mathbf{r})$, $\mu(\mathbf{r})$, and ϵ_{ij} are Lagrange multipliers. After a minimization and a unitary transformation we arrive at the one-particle equations

$$\left[-\frac{1}{2} \nabla^2 + \Lambda(\mathbf{r}) \right] \phi_i + \int \mu(\mathbf{r}') \frac{\delta \mathbf{X}}{\delta \phi_i^*(\mathbf{r})} d\mathbf{r}' = \epsilon_i \phi_i. \quad (21)$$

These generalized Kohn–Sham equations are much more complicated than the conventional equations.

If the ensemble quantities \mathbf{X} are constants, i.e., do not depend on \mathbf{r} , the following direct method can be applied: the total ensemble energy and from it the Kohn–Sham potential are directly constructed with fixed value of \mathbf{X} . Then one does not have to use the Lagrange multipliers and the Kohn–Sham equations have the usual form. But we have different Kohn–Sham potential and equations for every value of \mathbf{X} :

$$\left[-\frac{1}{2} \nabla^2 + v_{KS}^{\mathbf{X}}(\mathbf{r}) \right] \phi_i^{\mathbf{X}} = \epsilon_i^{\mathbf{X}} \phi_i^{\mathbf{X}}. \quad (22)$$

This direct method is illustrated for atomic multiplets in the following section.

IV. APPLICATION TO ATOMIC MULTIPLETS

Using equal weighting factors for a spherically symmetric system, the ensemble noninteracting kinetic energy is given by

$$T_s = \sum_{j=1}^N \lambda_j \int P_j \left[-\frac{1}{2} P_j'' + \frac{l_j(l_j+1)}{2r^2} P_j \right] dr, \quad (23)$$

where P_j and λ_j are the radial ensemble orbitals and the occupation numbers corresponding to the given configuration, respectively. " denotes second derivative with respect to r . The radial ensemble density has the form

$$\varrho = \sum_{j=1}^N \lambda_j P_j^2. \quad (24)$$

What can we choose for the extra variables? While the current densities generally are different from zero the ensemble current density

$$\mathbf{j} = \sum_{\gamma} w_{\gamma} \mathbf{j}_{\gamma} \quad (25)$$

is zero if the weighting factors are all equal.

Instead we can select the angular momenta L^2 and S^2 . Here we do not give the expectation value of the operators L^2 and S^2 with the orbitals and minimize them using Lagrange multipliers. Instead a direct method is proposed. L^2 and S^2 are constants of motion and the total ensemble energy can be given by

$$E^{LS} = E^{LS}[P_i^{LS}]. \quad (26)$$

It can also be written as

$$E^{LS} = E_{av} + \sum_j C_j^{LS} B_j^{LS} + E_c^{LS}, \quad (27)$$

where E_{av} is the average energy of the different multiplets corresponding to a given configuration. The second term in the right-hand side of Eq. (27) is responsible for the multiplet separation and E_c^{LS} is the correlation energy. Textbooks (see, e.g., Ref. 6) provide several methods for obtaining the expression $\sum_j C_j^{LS} B_j^{LS}$ from determinants spanning the noninteracting subspace corresponding to LS . The explicit form of Eq. (27) for the p^2 electron configuration:⁶

$$E(^3P) = E_{av} - \frac{3}{25} F^2(pp), \quad (28)$$

$$E(^1D) = E_{av} + \frac{3}{25} F^2(pp), \quad (29)$$

$$E(^1S) = E_{av} + \frac{12}{25} F^2(pp). \quad (30)$$

$F^2(pp)$ is the Slater integral,

$$F^2(pp) = \int \int R_{2p}^2(r_1) R_{2p}^2(r_2) \frac{r_{<}^2}{r_{>}^3} dr_1 dr_2, \quad (31)$$

where R_{2p} is the radial wave function of the $2p$ electrons. $r_{<}$ means r_1 if it is smaller than r_2 and r_2 if it is smaller than r_1 , and $r_{>}$ is the greater of r_1 and r_2 .

As E^{LS} is a functional of the ensemble radial wave functions P_i^{LS} ,

$$E^{LS} = E^{LS}[P_i^{LS}], \quad (32)$$

the OPM (Ref. 7) or KLI (Ref. 8) methods can be applied. Here the KLI method is used. Then the Kohn–Sham equations have the form

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l_i(l_i+1)}{r^2} + v_{KS}^{LS} \right) P_i^{LS} = \epsilon_i^{LS} P_i^{LS}. \quad (33)$$

The Kohn–Sham potential

$$v_{KS}^{LS} = v + v_J^{LS} + v_x^{LS} + w^{LS} + v_c^{LS}, \quad (34)$$

where v_x^{LS} and v_c^{LS} are the exchange and the correlation potentials and the potential w^{LS} is responsible for the multiplet separation. The generalization of the KLI method leads to the accurate approximations,⁹

$$v_x^{LS} = v_s^{LS} + \sum_i (\epsilon_i^{LS} - \epsilon_i^{LS}) |k_i^{LS}|^2 \quad (35)$$

and

$$w^{LS} = \sum_i (k_i^{LS})^2 w_i^{LS} = \sum_i (k_i^{LS})^2 \sum_j C_j^{LS} \frac{1}{P_i^{LS}} \frac{dB_j^{LS}}{dP_i^{LS}}, \quad (36)$$

where v_s^{LS} is the Slater potential

$$v_s^{LS}(\mathbf{r}) = -\frac{1}{2} \int d\mathbf{r}' \varrho^{LS}(\mathbf{r}') \left| \sum_j k_j^{LS}(\mathbf{r}') k_j^{LS}(\mathbf{r}) \right|^2 / |\mathbf{r} - \mathbf{r}'|. \quad (37)$$

The functions k_i^{LS} are defined with

TABLE I. Hartree–Fock, generalized KLI with local Wigner correlation functional (this work) and experimental total energies for the multiplets 3P , 1D , and 1S of the C, O, S, and Si atoms (in Rydberg).

		C	O	Si	S
3P	HF	−75.3772	−149.6187	−577.7085	−795.0095
	KLI+LW	−75.6934	−150.1166	−578.7458	−796.2406
	Expt.	−75.6904	−150.1346	−578.7500	−796.2780
D	HF	−75.2626	−149.4584	−577.6300	−794.9042
	KLI+LW	−75.5940	−149.9805	−578.6800	−796.1577
	Expt.	−75.5979	−149.9900	−578.6926	−796.1938
1S	HF	−75.0991	−149.2219	−577.5169	−794.7489
	KLI+LW	−75.4785	−149.8105	−578.5725	−796.0199
	Expt.	−75.4931	−149.8267	−578.6097	−796.0759

$$P_i^{LS} = (\varrho^{LS})^{1/2} k_i^{LS}, \quad (38)$$

where ϱ^{LS} is the radial electron subspace density. $(\epsilon_i^{LS} - \epsilon_i^{LS})$ are the differences between the Kohn–Sham and the Hartree–Fock one-electron energies,

$$\epsilon_i^{LS} - \epsilon_i^{LS} = \langle \phi_i | v_x^{LS} | \phi_i \rangle - \langle \phi_i | \hat{v}_x^{HF} | \phi_i \rangle, \quad (39)$$

where \hat{v}_x^{HF} is the Hartree–Fock exchange potential taken with the density functional orbitals.

V. RESULTS AND DISCUSSION

There is one unknown term in the Kohn–Sham potential (34); therefore one has to use an approximation for the correlation potential v_c^{LS} . Here, a simple local Wigner type expression is applied.¹⁰ The local Wigner correlation energy is

$$E_c^{LW}[n] = \int \frac{an}{b + r_s} d\mathbf{r}, \quad (40)$$

where r_s is the Wigner–Seitz radius,

$$r_s = (3/4\pi n)^{1/3}. \quad (41)$$

The parameters a and b depend on L and S .

As an illustration total energies and multiplet separation for C, O, Si, and S atoms are presented in Tables I and II. The results of the present method are denoted by KLI+LW. For comparison the Hartree–Fock and experimental values

TABLE II. Hartree–Fock, generalized KLI with local Wigner correlation functional (this work), and other calculated and experimental total energy differences of the terms 1D and 1S from the 3P (in Rydberg) for the C, O, S, and Si atoms.

		C	O	Si	S
$^3P-^1D$	HF	0.1146	0.1603	0.0785	0.1053
	KLI+LW	0.0994	0.1361	0.0658	0.0829
	Expt.	0.0929	0.1446	0.0574	0.0842
	Other calculations	0.1000	0.1520		
$^3P-^1S$	HF	0.2782	0.3968	0.1916	0.2606
	KLI+LW	0.2149	0.3061	0.1733	0.2207
	Expt.	0.1973	0.3079	0.1403	0.2021
	Other calculations	0.2100	0.3212		

are also shown. We applied the following parameters: $a = -0.028\,592$, $b = 0.2679$ for 3P , $a = -0.032\,997$, $b = 0.340$ for 1D , and $a = -0.068\,263$, $b = 1.0658$ for 1S . Though the local Wigner expression is a very simple approximation, the KLI+LW method results in considerable improvement.

Table II presents multiplet separation. For comparison the multiplet separation obtained by Bagus and Bennett¹¹ for the C atom and Moser and Nesbet¹² for the O atom are also presented. These data were obtained by configuration interaction and Bethe–Goldstone calculations. The present method leads to results of similar quality. We have to emphasize that the correlation potential applied here is the simplest possible local form that satisfy important coordinate-scaling requirements.^{13–15}

The KLI method is a very powerful approach. However, it is a very delicate problem to find an appropriate correlation functional, i.e., a correlation functional that performs well together with the KLI exchange. In the existing approximating functionals exchange and correlation are treated together and if we change only the exchange part (into KLI) the balance between the exchange and correlation is ruined and we might receive worse results than in the exchange-only case.⁹ Gross and co-workers¹⁶ found that among the existing correlation functional the Colle–Salvetti correlation functional is the best. In a lot of cases KLI+Colle–Salvetti gives results better than any other existing functional. However, the multiplet separation obtained by KLI+Colle–Salvetti is worse than the exchange-only KLI.¹⁷ The study of correlation leading to correct multiplet separation is a challenge for future research. Our present approach is the first promising step in that direction.

In summary, the generalization of density functional theory presented here provides a systematic way of treating multiplets. The generalized KLI method with a simple local Wigner correlation functional leads to excellent total and multiplet separation energies.

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